Progress in inorganic cathode catalysts for electrochemical conversion of carbon dioxide into formate or formic acid

Dongwei Du [a], Rong Lan [a], John Humphreys [a] and Shanwen Tao [a,b*]

[a] School of Engineering, University of Warwick, Coventry CV4 7AL, UK

[b] Department of Chemical Engineering, Monash University, Clayton, Victoria 3800, Australia

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ABSTRACT: As a greenhouse gas, carbon dioxide in the atmosphere is one of the key contributors to climate change. Many strategies have been proposed to address this issue, such as CO_2 capture and sequestration (CCS) and CO_2 utilization (CCU). Electroreduction of CO_2 into useful fuels is proving to be a promising technology as it not only consumes CO_2 but can also store the redundant electrical energy generated from renewable energy sources (e.g., solar, wind, geothermal, wave etc.) as chemical energy in the produced chemicals. Among all of products from CO_2 electro-conversion, formic acid is one of the highest value-added chemicals which is economically feasible for large-scale applications. This paper summarizes the work on inorganic cathode catalysts for the electrochemical reduction of CO_2 to formic acid or formate. The reported metal and oxide cathode catalysts are discussed in detail according to their performance including; current density, Faradaic efficiency and working potentials. In addition, the effects of electrolyte, temperature and pressure are also analyzed. The electroreduction of CO_2 to formic acid or formate is still at an early stage with several key challenges that need to be addressed before commercialization. The major challenges and the future directions for developing new electrocatalysts for the reduction of CO_2 to formic acid are discussed in this review.

Keywords: Review, Electrochemical synthesis, CO_2 utilization, CO_2 reduction, formic acid, formate, catalysts

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* Corresponding author:
School of Engineering, University of Warwick, Coventry CV4 7AL, UK
E-mail: S.Tao.1@warwick.ac.uk
Tel: +44 (0)24 761 51680
Fax: +44 (0)24 764 18922

1. Introduction

1.1. Background

It is generally believed that the rising amount carbon dioxide (CO_2) in the atmosphere is one of the key factors contributing to climate change, this is due to its effect as a greenhouse gas [1]. The concentration of CO_2 in the atmosphere has increased from 278 ppm before the industrial revolution to around 400 ppm at present (Fig. 1) [2]. The massive consumption of fossil resources in the global production of energy and the chemical industry are the major contributors to CO_2 accumulation [3-5]. A CO_2 circular economy chart presented by Centi's group is shown in Fig. 2 [6]. Nearly half of the energy is lost in the form of CO_2 during the transformation of fossil fuels to energy products or other raw materials. Even in the production of biofuels such as ethanol, large amounts of CO_2 is formed (around 1 ton CO_2 per ton ethanol). Therefore it is supposed that the current society is CO_2 centered instead of fossil fuel centered. Although CO_2 is a necessary nutrient for plant growth and an important raw material in many industrial processes, a series of concerns are currently being raised regarding its ability to increase global temperature through the greenhouse effect, and thereby lead to an increase in the water levels on the Earth's surface. It is predicted that the effects of climate change will last for up to 1000 years even if the current emission of greenhouse gases is halted [7]. As a consequence, the reduction of CO_2 released and conversion of CO_2 in to useful materials has become a significant challenge with many countries expanding financial investment due to the environmental and economic

benefits this new technology can bring.

In general, there are four methods to reduce the amount of CO_2 in the atmosphere [8]: (1) improving the efficiency of current energy processes; (2) using non-carbon or low carbon sources for energy generation; (3) CO_2 capture and sequestration (CCS); and (4) CO_2 utilization (CCU). From these options, the last two approaches seem to be the most direct and useful techniques that can be used to address the release of CO_2 to the atmosphere. However, since CCS involves the storage of the captured and sequestered CO_2 in geological sub surfaces or oceans, then there is still the potential that it will leak back in to the atmosphere. Therefore, CO_2 utilization seems to be the best approach in addressing the current issue. 80~85 % of the world energy consumption is provided by carbon-based fossil fuels [9]. Therefore converting CO_2 into useful fuels can not only decrease the CO_2 emissions but also reduce the demand on fossil fuels.

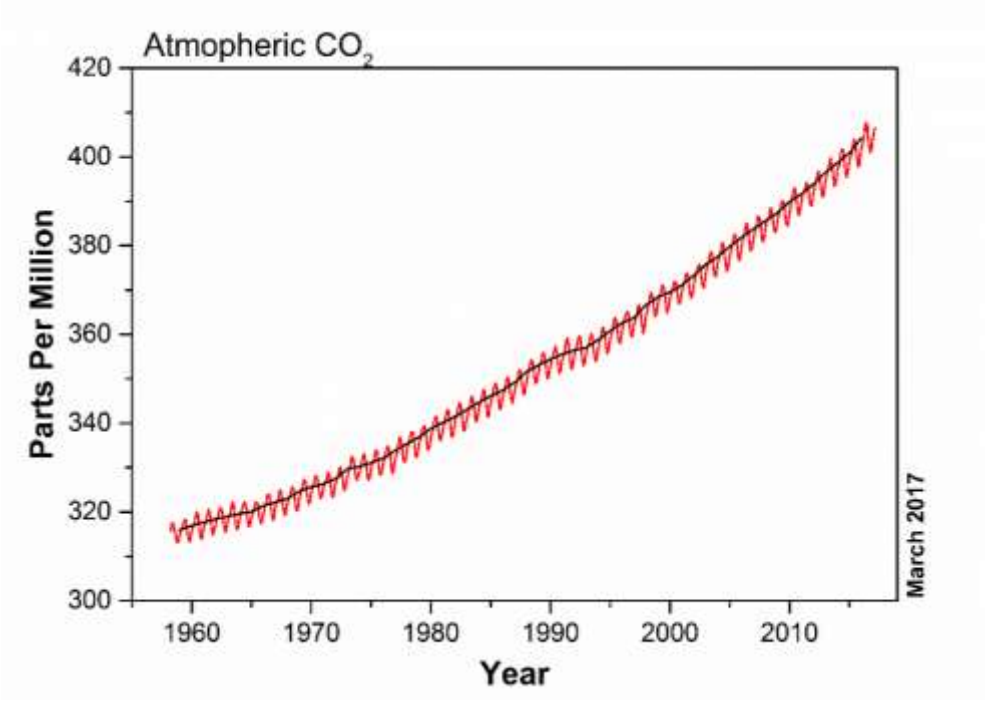

Fig. 1. CO_2 concentrations in the atmosphere form 1960 to 2016 [2].

Generally, CO_2 conversion can be grouped into four categories, namely, chemical methods [10-12], photocatalytic reduction [13, 14], biotransformation [15, 16] and electrocatalytic reduction [17-19]. The global annual CO_2 production was 40 Gt in 2014 with only a very small percentage of this recycled, meaning that the potential for further development in this field is huge [20]. Qiao *et al.* summarized the main barriers for large scale application of these technologies [21]: (1) high cost for CO_2 capture, separation and transportation; (2) high energy consumption during chemical or electrochemical reduction; (3) small market presently which is not attractive to invertors; (4) fewer industrial participation. Although there are numerous challenges on CO_2 reduction, it is still a promising and practical solution in order to relieve the environmental and energy issues currently faced.

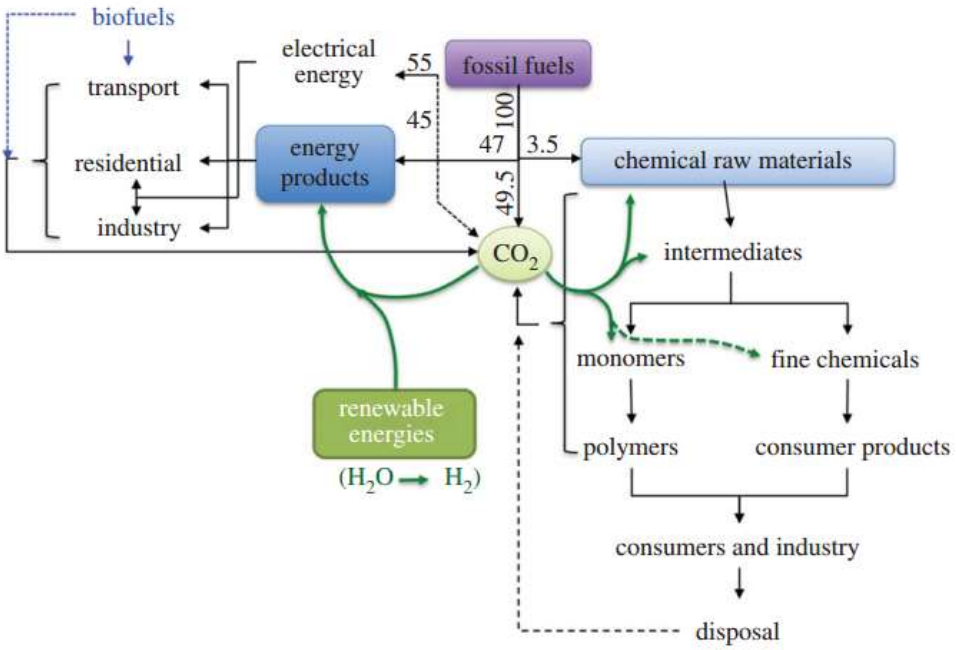

Fig. 2. A model of CO_2 circular economy and its impact on the chemical and energy value chain [6].

1.2. Current status of formic acid industry

Among the many products achieved from CO_2 reduction, formic acid is one of the most interesting due to a number of factors. Firstly, the economic possibility of large-scale electrochemical reduction of carbon dioxide to formic acid is considered to be feasible [8]. As shown in Fig. 3, formic acid is one of the highest value-added chemicals that can be produced from CO_2 reduction. The price for formic acid is around 1300 USD per ton, which is approximately the same as that of carbon monoxide, but much higher than that for methanol and ethylene [22].

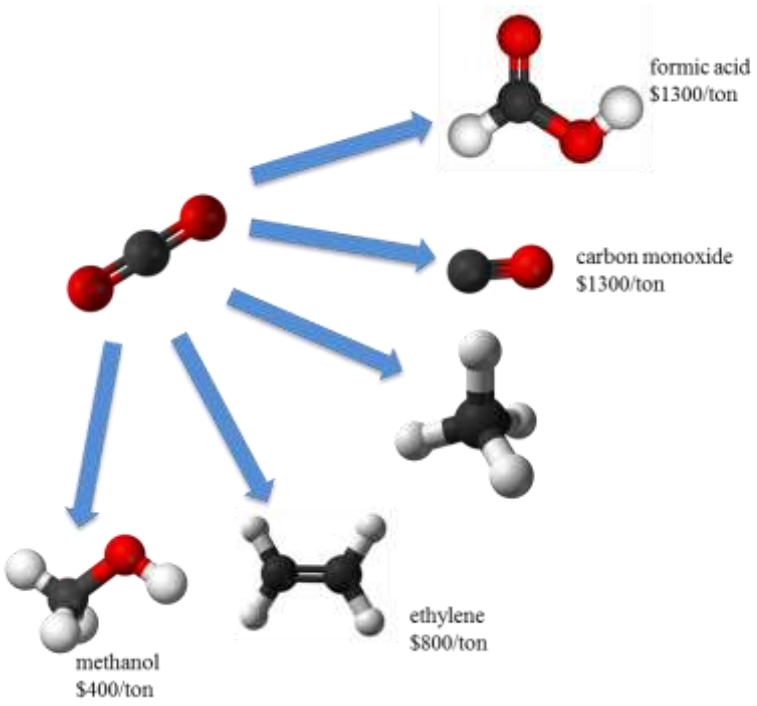

Fig. 3. Conversion of CO_2 into more valuable commodity chemicals.

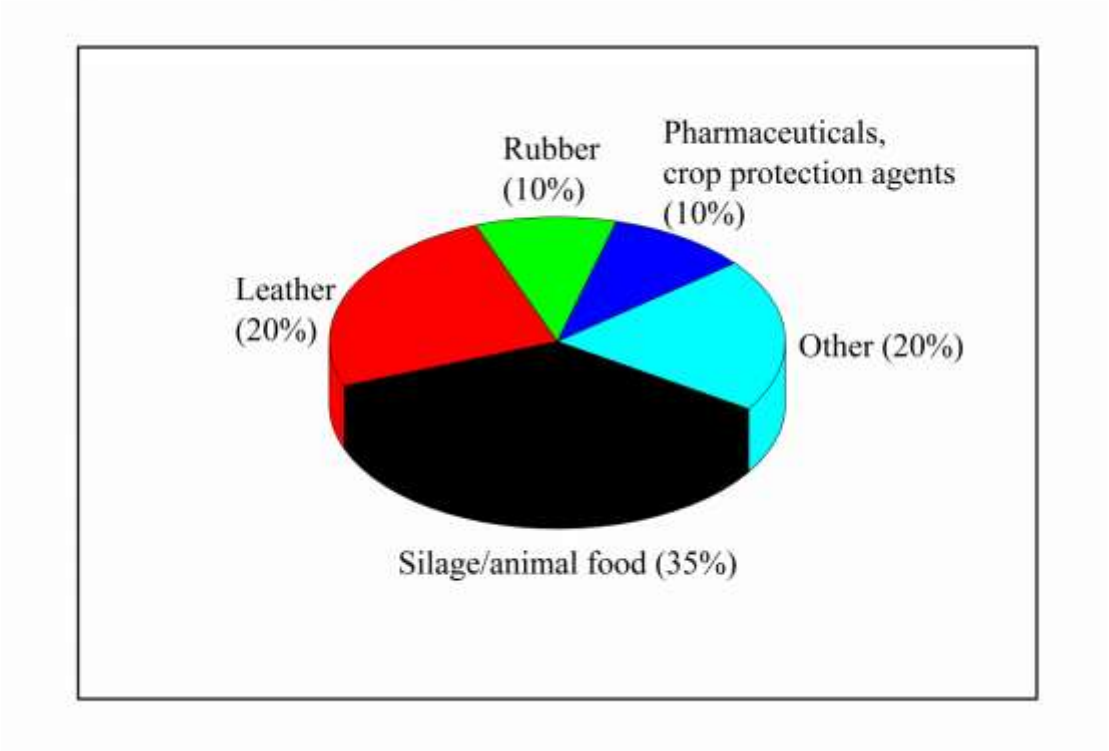

Fig. 4. Applications of formic acid [23].

Secondly, formic acid is the simplest carboxylic acid existing naturally, with its

demand dramatically expanding year by year due to its various applications. The global formic acid market is estimated to reach 620 million dollars by 2019 [5]. As shown in Fig. 4, a significant percentage of formic acid consumption is used in agriculture as a preservative due to its natural antibacterial properties. The addition of formic acid to the livestock feed not only greatly reduces the growth of bacteria but also promotes the fermentation processes thus lowering the fermentation temperature. In addition, more nutrients remain in the silage. In industry, formic acid is commonly used in the production of leather, manufacturing of rubber and dyeing of textiles since it evaporates without leaving any residue, unlike mineral acids.

Thirdly, formic acid has been proposed as a fuel for fuel cells [24-26] and is also a promising hydrogen carrier with a hydrogen content of 4.4 wt% [27, 28]. However, the energy density of formic acid is 2.1 kWh/liters which is less than half the value of methanol, and much less than other CO_2 derived products with higher C-chain such as alcohols, hydrocarbons and oxygenates [29-31], thereby limiting its application for portable and transport applications.

Additionally, formate treatment has been proven to be a more effective and environmentally friendly treatment for slippery roads than traditional salts and has been demonstrated in countries such as Switzerland and Austria.

Presently, there are four commercial routes for the production of formic acid: 1. Hydrolysis of methyl formate; 2. Oxidation of hydrocarbons; 3. Hydrolysis of formamide; 4. Acidolysis of alkali formates. The traditional routes used to synthesize formic acid are neither straightforward nor environment friendly [32]. Electrochemical

conversion from CO_2 to formic acid might therefore prove be a promising alternative synthesis method. More importantly, this sustainable process will reduce CO_2 emissions if the electricity is generated from renewable resources.

1.3. Electrocatalysis of CO_2

Energy generated from carbon-free sources such as renewable energy (e.g., solar, wind, geothermal, wave etc.) and nuclear energy are generally in the form of electricity; however, the places with a sufficient amount of these resources are usually far away from the areas with a high energy demand [33]. Therefore, storing the redundant electric energy in the form of chemical energy would help solve this energy imbalance. In this respect, CO_2 would be an ideal feedstock to convert into useful fuels for energy storage, while it would be possible to simultaneously transport the synthesized fuels to the users' sites. As a result, electrocatalysis of CO_2 has aroused great attention among many CO_2 conversion methods.

According to the number of electrons transferred per molecular of CO_2 during the reaction, the electrochemical reduction of CO_2 can be divided into one-, two-, four-, six- and eight-electron pathways in aqueous and non-aqueous electrolytes. The major products and their thermodynamic electrochemical half-reactions are shown in Table 1 [21]. It can be concluded that the main products are: one-electron, oxalic acid ($H_2C_2O_4$) or oxalate ($C_2O_4^{2-}$); two-electron, carbon monoxide (CO) [34-37] and formic acid (HCOOH) or formate ($HCOO^-$) [38, 39]; four-electron, formaldehyde (CH_2O); six-electron, methanol (CH_3OH) [40-43], ethylene (CH_2CH_2) [44, 45], and ethanol

(CH_3CH_2OH); eight-electron, methane (CH_4) [46, 47]. The reactions listed in Table 1 only indicate the thermodynamic property which is related to the possibility of a reaction, while kinetic information is not provided. These reactions proceed very slowly even when catalysts are applied. In addition, the products of electroreduction are commonly a mixture of the ones listed in Table 1 rather than a single product. In terms of the type of product and the amount of each component, they strongly dependant on a large number factors, including the kind of electrocatalyst, electrode type, electrolyte, pressure, temperature, cell configuration and applied potential [48]. Overall, the reaction system is very complicated and the end products are affected by many variables.

Table 1 Equilibrium potentials for various CO_2 electroreduction reactions(vs SHE) in aqueous solution, at 298K and 1.0 atm [21].

Thermodynamic electrochemical half-reactions	Electrode potentials (V vs. SHE)
$CO_2(g) + 4H^+ \rightarrow C(s) + 2H_2O(l)$	0.210
$CO_2(g) + 2H_2O(l) + 4e^- \rightarrow C(s) + 4OH^-$	-0.627
$CO_2(g) + 2H^+ + 2e^- \rightarrow HCOOH(l)$	-0.250
$CO_2(g) + 2H_2O(l) + 2e^- \rightarrow HCOOH(aq) + OH^-$	-1.078
$CO_2(g) + 2H^+ + 2e^- \rightarrow CO + H_2O(l)$	-0.106
$CO_2(g) + H_2O(l) + 2e^- \rightarrow CO + 2OH^-$	-0.934
$CO_2(g) + 4H^+ + 4e^- \rightarrow CH_2O(l) + H_2O\ (l)$	-0.070
$CO_2(g) + 3H_2O(l) + 4e^- \rightarrow CH_2O(l) + \ 4OH^-$	-0.898
$CO_2(g) + 6H^+ + 6e^- \rightarrow CH_3OH(l) + H_2O(l)$	0.016
$CO_2(g) + 5H_2O(l) + 6e^- \rightarrow CH_3OH(l) + 6OH^-$	-0.812
$CO_2(g) + 8H^+ + 8e^- \rightarrow CH_4(g) + 2H_2O(l)$	0.169

$CO_2(g) + 6H_2O(l) + 8e^- \rightarrow CH_4(g) + 8OH^-$	-0.659
$2CO_2(g) + 2H^+ + 2e^- \rightarrow H_2C_2O_4$(aq)	-0.500
$2CO_2(g) + 2e^- \rightarrow {C_2O_4}^{2-}$(aq)	-0.590
$2CO_2(g) + 12H^+ + 12e^- \rightarrow CH_2CH_2(g) + 4H_2O(l)$	0.064
$2CO_2(g) + 8H_2O(l) + 12e^- \rightarrow CH_2CH_2(g) + 8OH^-$	-0.764
$2CO_2(g) + 12H^+ + 12e^- \rightarrow CH_3CH_2OH(l) + 3H_2O(l)$	0.084
$2CO_2(g) + 9H_2O(l) + 12e^- \rightarrow CH_3CH_2OH(l) + 12OH^-$	-0.744

A few excellent review articles have reported on the electroredution of CO_2 in terms of the catalyst [49] and the conversion towards formic acid with regards to the aspects of reaction mechanisms [50], engineering, and economic feasibility [8]. There is a review on the electrochemical reduction of CO_2 to formic acid in terms of electrode structure, catalyst materials, electrolyte and cell design that has recently been published [51]. The production of formate by molecular electrocatalysts was also reviewed by Taheri *et al.* [52]. In this mini-review, we complementarily focus on the development and recent progress made on metal and metal oxide catalysts for the electrochemical reduction of carbon dioxide into formate or formic acid.

2. Electrochemical synthesis of formate and formic acid

As described above, the overall reaction in the production of formic acid is a combination of an oxidation and reduction reaction at anode and cathode respectively. Fig. 5 shows the basic configuration for electroreduction of CO_2 into formate/formic acid. During the electrolysis, side reactions always compete with formate/formic acid

production, leading to reduced faradaic and energy efficiencies. The most common side reaction is the electrolysis of water, during which hydrogen, instead of formic acid, is formed at the cathode. CO_2 electroreduction to formate/formic acid can take place at different pH values with the pH affecting the formed product. As the dissociation constant of formic acid is 1.6×10^{-4} at 298K (pk_a = 3.8), formic acid is produced when the pH is below 3 while formate is formed at a higher pH [53]. Most of the experiments that have been carried out so far have used an alkaline electrolyte, therefore the electrochemical reactions are presented as follows.

Anode:

$$2OH^- \rightarrow H_2O + \frac{1}{2}O_2 + 2e^- \quad (1)$$

(or $H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-$ in acidic conditions)

Cathode:

$$CO_2(aq) + H_2O + 2e^- \rightarrow HCOO^-(aq) + OH^- \quad (2)$$

(or $CO_2(aq) + 2H^+ + 2e^- \rightarrow HCOOH(aq)$ in acidic conditions)

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2(g) \quad (3)$$

(or $2H^+ + 2e^- \rightarrow H_2(g)$ in acidic conditions)

Equation 3 is more thermodynamically favorable than equation 2. In order to achieve a high selectivity for formic acid/formate, the development of proper catalysts is required to kinetically suppress the hydrogen evolution. Normally, the major catalysts for CO_2 electroreduction to formic acid/formate are related to the following elements In, Pb, Sn, Hg and Zn.

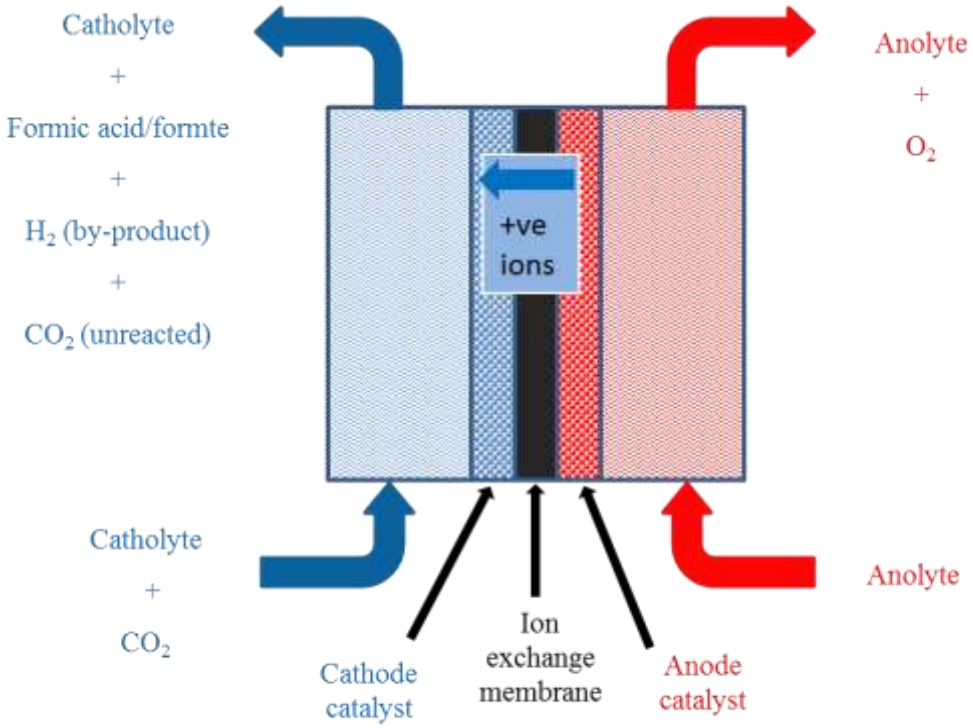

Fig. 5. Schematic diagram of electro-conversion of CO_2 into formate/formic acid.

2.1. Applied cathode materials

2.1.1. Lead (Pb) based catalysts

In 1998, Kaneco *et al*. investigated a lead wire electrode in the electroreduction of CO_2 to formic acid at ambient temperature and pressure [54]. A KOH/methanol-based electrolyte was applied in their experiments due to the high CO_2 solubility in methanol. At ambient temperature and pressure, the CO_2 solubility is about five times larger in methanol than in water [55], the CO_2 solubility in this system was also promoted by bicarbonate ions formed from CO_2 and KOH. The results showed that the highest Faradaic efficiency of formic acid was 66% at -2.0V vs. Ag/AgCl (sat. KCl) with a current density of 4 mA cm^{-2}. The remaining products obtained were CO and H_2. The

GC-MS studies explored the mechanism of CO_2 to formate and CO as shown in Fig. 6.

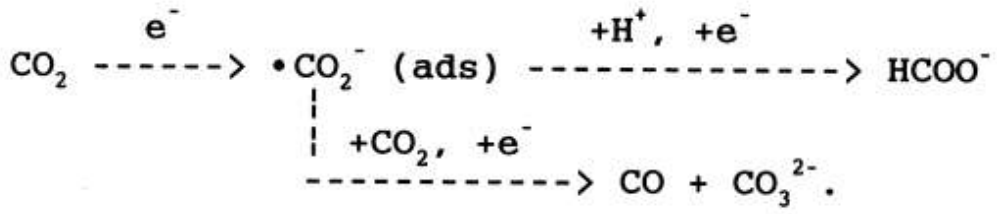

Fig. 6. The pathway by which formic acid and CO are formed is as follows [55].

Köleli and Balun prepared Pb-granule electrodes in a fixed-bed reactor to convert CO_2 to formic acid in 0.2 M aqueous K_2CO_3 solution [56]. The maximum Faradaic efficiency of 94 % was obtained at -1.8 V (vs. SCE), 50 bar and 80 ^oC. They found that the Faradaic efficiency and current density significantly depended on the applied potential, pressure and temperature. Specifically, at the same temperature and pressure, the Faradaic efficiency firstly increased and then decreased between -1.6 to -2.2 V (vs. SCE), reaching the peak point at -1.8V (SCE). At this optimal electrolysis potential, the Faradaic efficiency and current density went up as the pressure increased, e.g., it was ca. 0.5 mA cm^2 with 39% under 1 bar and 0.7 mA cm^2 with 76% under 40 bar at 25 ^oC. Generally, an increase in temperature should lead to a decrease in Faradaic efficiency for formate due to the decreased CO_2 solubility at high temperature; however, no decrease was observed in that experiment as the temperature was increased from 25 to 80 ^oC. The Faradaic efficiency reached its highest value at 80 ^oC, with a possible reason for this being that temperature is the rate-limiting element under high pressure. Subramanian *et al.* electrodeposited lead on a stainless steel (SS 316) woven wire mesh substrate which was used as the cathode while using IrO_2/Ta_2O_5 film as the anode for

electrochemical reduction of CO_2 [32]. A flow type reactor was fabricated with 0.2 M potassium phosphate buffer solution and 0.2 M potassium hydroxide fed to the cathode and anode chambers respectively. The reaction was carried out at different current densities and catholyte feed rates. Results showed that the highest Faradaic efficiency of formate production was 93% at a flow rate of 3.2 mL min^{-1} and a current density of 2 mA cm^{-2} when the applied cell voltage ranged from 1.4 to 1.7 V. In addition to the stainless steel substrate, different kinds of substrate have been used. Honeycomb-like porous Pb was prepared by electrodeposition at a copper plate [57]. The surface area was enlarged by the porous structure thus enhancing the catalytic ability for CO_2 reduction, obtaining a faradaic efficiency of 96.8% at -1.7V versus SCE at 5 ^oC in 0.5M $KHCO_3$. Kwon and Lee synthesized a nanolayered Pb electrode on Pt quartz crystal by employing a stepwise potential deposition method [58]. It was found that more active Pb crystallinity was formed for the formate production.

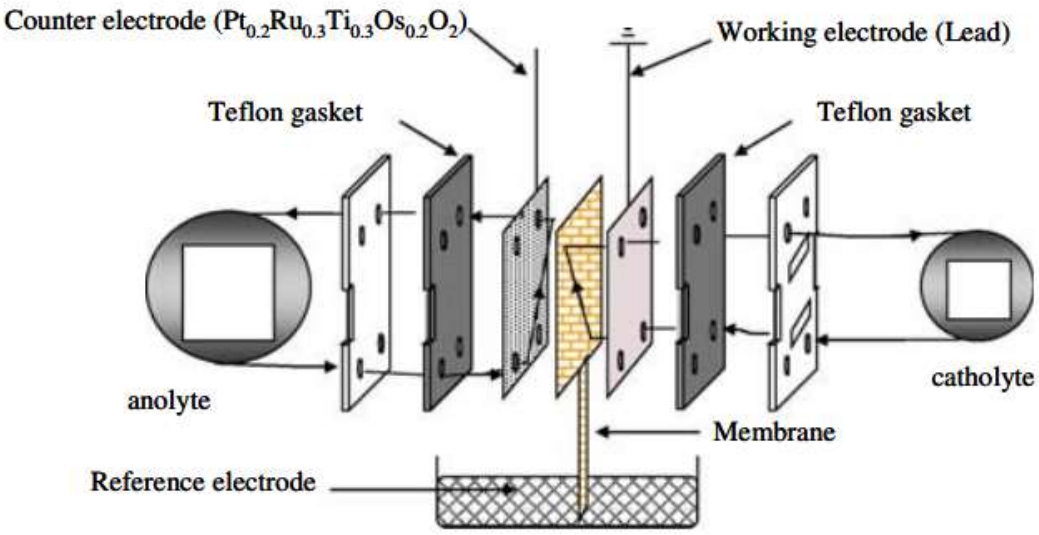

Fig. 7. Scheme of the filter press cell used to perform the electrochemical measurements

[39].

In 2009, a lead plate was applied in a filter-press cell (Fig. 7) for electro-reduction of CO_2 [39]. 0.5 M sulphuric acid solution and 0.5 M sodium hydroxide were pumped to the anode and cathode respectively. The cyclic voltammetry test suggested that the reaction was mostly controlled by diffusion. The results also showed that the Faradaic efficiency of formate strongly depended on the pH and the electrode potential. The best performance was obtained in the pH range of 7–9 at -1.6 V vs. SCE. In addition, the temperature of the electrolyte was also a significant parameter determining the selectivity towards formate. It increased up to 90% when the temperature decreased from 20 to 4 ^{o}C. Similarly, the same device was used to study the influence of the other variables [59]. The results revealed that the current density and electrolyte flow rate affected the performance of this continuous system. The rate of formate production was improved when the current density was increased up to 10.5 mA cm^{-2}. However, any further increase of the current density did not promote formate production and caused a drop in Faradaic efficiency. This could be attributed to the improved evolution of H_2. Results also indicated that mass transport limited a further increase of formate due to current density. At a higher catholyte flow rate, the performance was restricted by the adsorption and desorption in the lead cathode surface.

Lee and Kanan's study demonstrated that Pb film obtained through the reduction of PbO_2 exhibited up to 700-fold lower H^+ reduction activity than a Pb foil while not compromising its activity for CO_2 reduction to formate [60]. Moreover, the oxide-

derived Pb could perform with a high selectivity for CO_2 conversion into formate, even at very low CO_2 concentrations in a N_2-saturated $NaHCO_3$ solution. It was supposed that the coverage of a thin layer which can block the H^+ reduction and catalyze CO_2 reduction is much higher on the oxide-derived Pb electrode than that on Pb foil. The mechanisms of high selectivity for formate over CO and H_2 on Pb were investigated by Jung's group [61]. They suggested a proton-coupled electron transfer mechanism via a formate intermediate (*OCHO) which was consistent with the observations, specifically, the strong O affinity, weak C-species binding and *H of Pb catalyst jointly contributed to the high selectivity for formate production and suppression of H_2 production.

2.1.2. Tin (Sn) based catalysts

Tin and its oxides have been widely reported as excellent cathode materials for the electrochemical reduction of CO_2 to formate/formic acid.

Lv *et al*. employed tin foil as the working electrode in a $KHCO_3$ solution with an undivided cell [62]. The formate product was determined by ion chromatography and titration. The Faradaic efficiency was up to 91% at -1.8 V vs Ag/AgCl while it gradually decreased with increasing electrolysis time due to the oxidation of formate at the anode (Fig. 8). The situation was more obvious when the formate concentration reached a high level (e.g., > 0.034 mol L^{-1}). The stability of the Tin electrode was shown to be good as it kept a stable current density of 2.5 mA cm^{-2} over 40h after which no impurities were found via EDS spectra.

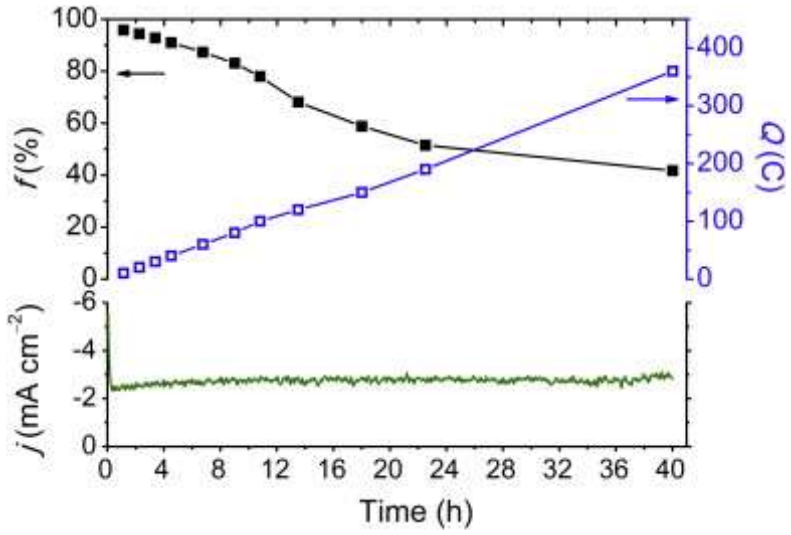

Fig. 8. Variations of the Faradaic efficiency for producing formate (■), the charge passed (□) and the current density with electrolysis time during the electrochemical reduction of CO_2 in 0.1 mol L^{-1} $KHCO_3$ solution at −1.8 V vs. Ag/AgCl for 40 h [62].

Anode oxidation of formed formic acid is a potential problem for the electrochemical reduction of CO_2. Zhang *et al*. developed a practical method to solve this problem [63]. Specially, the anode was coated with a Nafion film on the surface, which blocks the diffusion of formate onto it (Fig. 9). The results showed significant improvement on the performance: the Faradaic efficiency decreased from 90.3% to 78.5% when the charge passed from 50 C to 500 C on a coated anode; while on the naked anode, the Faradaic efficiency rapidly decreased from 89.2% to 35.3% under the same conditions.

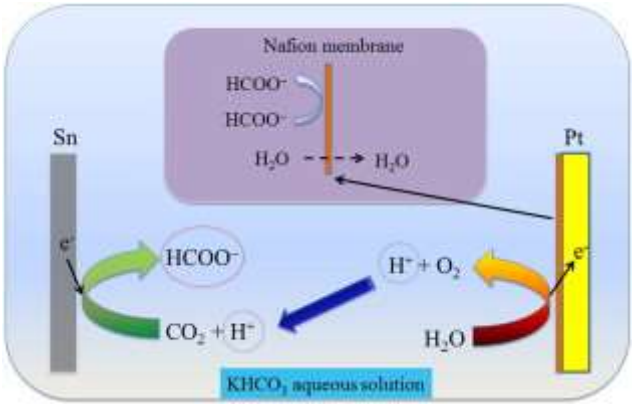

Fig. 9. Schematic of electrochemical reduction of CO_2 on Sn cathode and Pt@Nafion

anode [63].

Besides tin foil, other types of tin electrode have been employed in CO_2 reduction [64, 65]. Wu *et al.* concluded the change of morphology and the corresponding Faradaic efficiency on the Sn particles gas diffusion electrode (GDE) during long term electrolysis [64]. The GDE was made of 100 nm Sn particles with a loading of 2 mg cm^{-2} and then operated at -2.0 V vs. Ag/AgCl at room temperature and pressure. The original Sn particles were pulverized into irregularly shaped 30-40 nm particles after 3 hours, and the size continuously decreased to about 3 nm after 42.5 hours and remained at this level until 60 hours. When it comes to the Faradaic efficiency towards formate formation, it degraded from 90% to 81% during the first 10 hours, dropping to 56% after 60 hours. The decrease of the formate selectivity can be attributed to the reduced cathode potential and aggregation of fractured Sn particles. The total current density was stable at 17 mA cm^{-2}. Using the similar cell system, Prakash *et al*. found that a Nafion coated Sn powder GDL electrode performed with a high current density and Faradaic efficiency [66]. Namely, a current density of 27 mA cm^2 with a Faradaic efficiency of 70% was reached at -1.6 V vs. NHE. Basically, Sn GDEs for CO_2 electroreduction suffer from poor catalyst utilization as well as high costs. Wang *et al.* developed a novel method to overcome these weaknesses [67], in this method the Sn GDE consisted of a roll-pressed GDL with PTFE binder and a sprayed Sn catalyst layer with a Nafion binder. Although the performance of this electrode was not improved by much compared to the Nafion-GDE with Sn catalyst, the fabrication cost was

dramatically decreased to 8% of its original cost.

Combining tin with graphene is a good strategy to improve the CO_2 reduction performance. Lei *et al.* constructed tin quantum sheets confined in a graphene catalyst which provides a 9 times larger CO_2 adsorption capacity relative to bulk tin [68]. In 2014, Zhang *et al*. reported nanostructured tin catalysts for electrochemical reduction of CO_2 to formate [69]. The high surface area catalyst was made in two steps. Firstly, the graphene supported nano-SnO_2 was prepared via a facile hydrothermal method. Secondly, the obtained materials were loaded on glassy carbon electrodes. Before testing, the SnO_x was reduced through linear sweep voltammetric (LSV) scans. The results showed that in an aqueous $NaHCO_3$ solution, the maximum Faradaic efficiency for formate was over 93% at an optimal potential of – 1.8 V vs. SCE. Moreover, the current density reached as high as 10.2 mA cm^{-2} while also maintaining a good stability. The following possible mechanism for the reaction was proposed.

$$CO_2(solution) \rightarrow CO_2(ads) \quad (4)$$

$$CO_2(ads) + e^- \rightarrow {CO_2}^{\cdot -}(ads) \quad (5)$$

$${CO_2}^{\cdot -}(ads) + {HCO_3}^- \rightarrow {HCO_2}^-(ads) + {CO_3}^{2-} \quad (6)$$

$${HCO_2}^-(ads) \rightarrow {HCO_2}^-(solution) \quad (7)$$

$${CO_3}^{2-} + CO_2 + H_2O \rightarrow 2{HCO_3}^- \quad (8)$$

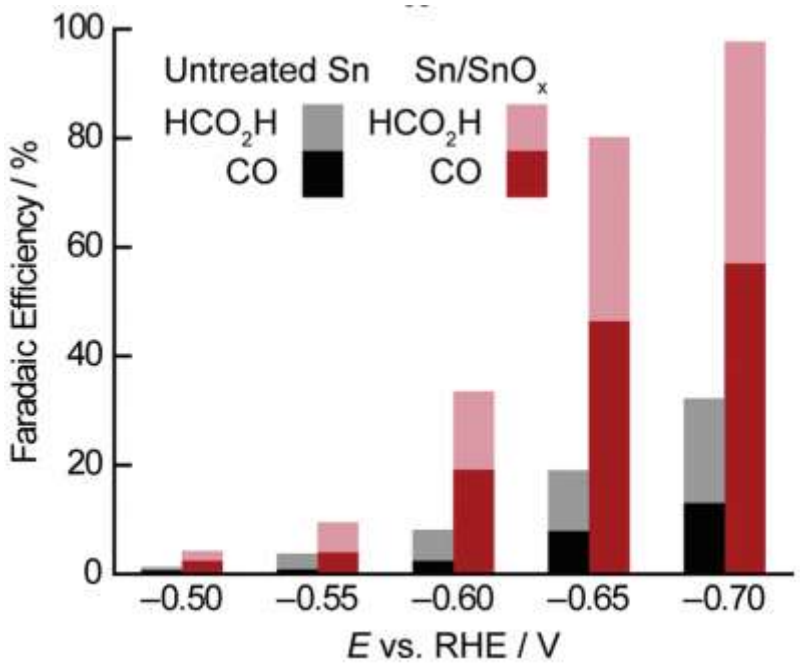

Fig. 10. Faradaic efficiency for HCO_2H and CO at various potentials. H_2 formation accounts for the remainder of the current [38].

In a recent report, electro-deposited Sn catalysts were used and it was found that the Faradaic efficiency to formate was greatly related to the deposition current density [70]. The optimized deposition current density for Sn fabrication was 15 mA cm^{-2}, on which the Faradaic efficiency of CO_2 conversion was over 91% at -1.4 V vs. SCE with a current density of ~ 1.5 mA cm^{-2}. In our study, nano-porous Sn foam deposited on Sn foil was used as the cathode. The maximum Faradaic efficiency for formate production reaches above 90% with a current density over 23 mA cm^{-2} [71]. It has been reported that electroposited Sn on Cu foil also exhibits good catalytic properties for CO_2 reduction. A maximum faradaic efficiency of 91.5% was obtained at -1.8 V vs. Ag/AgCl on the Sn/Cu electrode possessing a ~325 nm thick Sn-based film which was prepared by electrodeposition for 15 min [72]. Both Sn and Pb show good selectivity

towards formate. Sn-Pb alloy was also deposited onto carbon paper and a Sn−Pb alloy including a surface composition of $Sn_{56.3}Pb_{43.7}$ was shown to exhibit the highest Faradaic efficiency of 79.8% with the highest partial current density of 45.7 mA cm^{-2} [73]. However, formation of non-conductive PbO on the surface was a potential problem. Contrary to PbO, it was found that tin oxides (SnO_x) can greatly improve the performance on Sn electrodes for CO_2 reduction [38]. A thin film electrode was prepared by electrodeposition of Sn and SnO_x on a Ti foil substrate. This type of electrode exhibited a Faradaic efficiency around 4 time higher when compared with an untreated tin foil electrode at -0.7 V vs RHE (Fig. 10). Recently, Wu *et al*. also investigated the effect of thickness of the SnO_x layer on CO_2 reduction with a Sn electrode in a proton exchange membrane fuel cell (PEMFC) [74]. The 100 nm Sn nanoparticles were annealed at different temperatures and times, forming oxide layers ranging from 3.5 to 16 nm on the surface. Then the GDE was made based on the received Sn nanoparticles. The current density exhibited a negligible dependence on the thickness of the oxide layer while the selectivity of formate and CO demonstrated a strong relationship with oxide thickness (Fig. 11). A comparative study has been carried out on the electrocatalytic reduction of CO_2 to HCOOH in aqueous $KHCO_3$ solution with tin-oxide particles on multi-walled carbon nanotubes prepared through a variety of methods from $SnCl_2$ or $SnCl_4$ precursors [75]. It was found that SnO_x prepared from $SnCl_2$ exhibited a higher Faradaic efficiency (64%). The possible reason is that a $SnCl_2$ versus $SnCl_4$ precursor favors retention of the Sn(II) valence state in the surface layer. It seems low valent Sn is in favor of formic acid production, however, Sn

metal still shows a higher selectivity and partially oxidized Sn exhibits a higher activity than Sn itself. Recently, a catalyst for CO_2 reduction composed of 3D mesoporous SnO_2 nanosheets on carbon cloth was synthesized through a hydrothermal method [76]. A current density as high as 45 mA cm^{-2} was achieved with the Faradaic efficiency over 87% at -1.6V vs. Ag/AgCl. This excellent performance could be attributed to the large surface area generated by the highly porous structure. Kumar *et al.* prepared porous SnO_2 nanowires for the electroreduction of CO_2 into formate [77]. A relatively low overpotantial and high faradaic efficiency were reached due to the high density of grain boundaries from the porous structure.

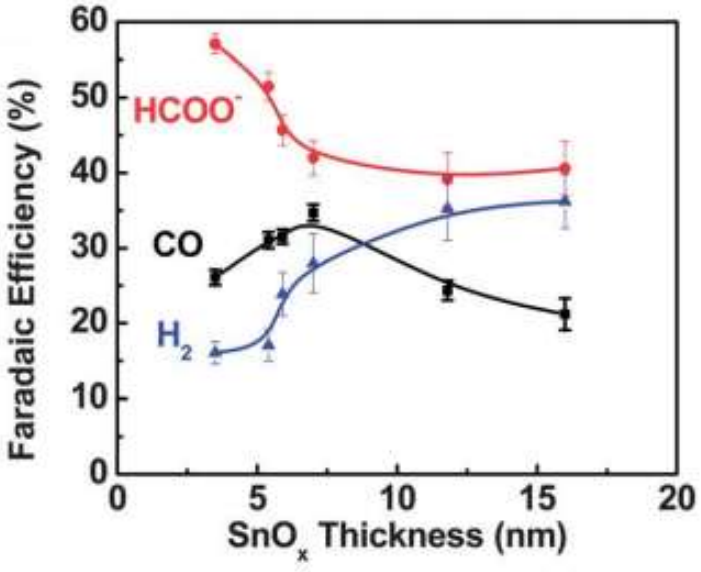

Fig. 11. CO_2 reduction electrolysis data at a cell potential of -1.2 V for Sn GDEs made of the as-received and annealed Sn nanoparticles. Faradaic efficiencies of CO, H_2 and $HCOO^-$ versus thickness of SnO_x layer [74].

2.1.3. Indium (In) based catalysts

Indium has been proven to have good catalytic activity with a high selectively for formic acid/formate in CO_2 electroreduction [78-80]. As early as 1983, Kapusta and Hackerman found that the current efficiency for CO_2 reduction to formate reached 95% on an indium electrode, however, the overall energy efficiency was very low due to the high over-potential of the reaction [78]. The same conclusion was obtained when a current density of 5.0 mA cm^{-2} was applied on an indium electrode in 0.5 mol L^{-1} $KHCO_3$ [79]. Over 93% of the current was converted to formate while the remaining current produced small amounts of CO and H_2. Ikeda *et al*. investigated CO_2 reduction in a 0.1 mol L^{-1} TEAP electrolyte with an In electrode [80], they demonstrated that at -2.0 V and -2.4 V vs. Ag/AgCl, the Faradaic efficiency of formic acid was around 85%. In addition to the aqueous electrolyte, ionic liquids are more attractive in CO_2 capture and conversion due to their higher CO_2 solubility and electrical conductivity [34, 81, 82]. Watkins and Bocarsly studied the performance of indium, tin and lead disc working electrodes for CO_2 reduction in a room temperature ionic liquid, 1-ethyl-3-methylimidazolium trifluoroacetate [Emim][TFA] [83]. It was indicated that [Emim][TFA] with 33% water as a co-solvent was an effective medium for converting CO_2 to formate (Fig. 12). The Faradaic efficiency reached over 90% at -1.9 V vs. Ag/AgCl and the production of formate was up to 3 $mgh^{-1}cm^{-2}$. The high current density and low electrode potential could be attributed to the stabilizing effect of the ionic liquid on the carbon dioxide intermediate and the increased solubility of carbon dioxide in the matrix. Compared to Sn and Pb, the cost of In would be high while only exhibiting similar activities as Sn and Pb to the electrochemical reduction of CO_2 to formate / formic acid.

From this point of view, it is not a favorable cathode catalyst.

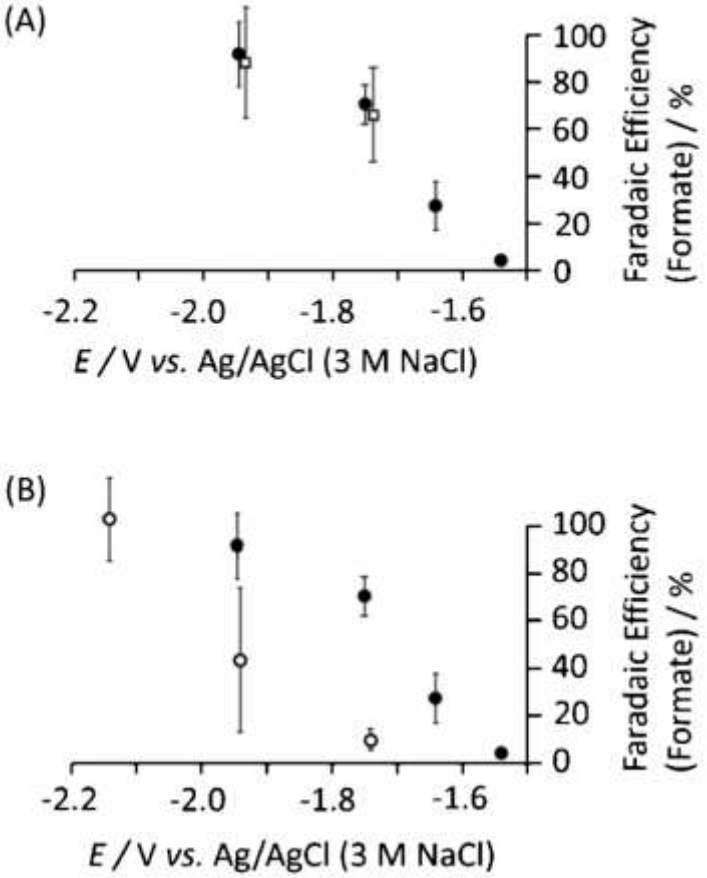

Fig. 12. (A) Comparison of tin (open squares) and indium (closed circles) electrodes for the Faradaic efficiency of formate production from carbon dioxide in a matrix of 2 mL [Emim][TFA] + 1mL D_2O (pD 6.7) at various applied potentials. (B) Comparison of lead (open circles) and indium (closed circles) electrodes for the Faradaic efficiency of formate production from carbon dioxide in a matrix of 2 mL [Emim][TFA] + 1mL D_2O (pD 6.7) at various applied potentials [83].

2.1.4. Zinc(Zn) based catalysts

Zn was also reported as a cathode for the electrochemical reduction of CO_2 to formic acid. Pt was used in almost all of the CO_2 electroreduction experiments as the counter

electrode. Pt is considered to be insert in general; however, it was found that Pt anodes could be dissolved at high anodic potentials and that the Pt cations can be reduced at the cathode after diffusion [84, 85]. This may affect the activity of the cathode catalysts. Yadav and Purkait firstly applied Co_3O_4, a cheap and easily available material as the anode, in which Zn was the electrocatalyst to generate formic acid [86]. Both Zn and Co_3O_4 were prepared through the electrodeposition method. In their two electrode system, the maximum Faradaic efficiency was 78.54% in $KHCO_3$ solution at 1.5 V. The authors also compared the catalytic activity of the Zn cathode with Sn and it was found that the activity of Zn was slightly lower [87]. In this respect, Sn is still a better choice although the cost of Zn is lower.

2.1.5. Copper (Cu) based catalysts

Normally, the primary product of CO_2 electrochemical reduction on copper is methane [44, 47, 88-90], although some researchers found that a small percentage of formic acid could be produced during the electrolysis process [91-93]. Sen *et al*. prepared a copper nanofoam electrode which exhibits a high Faradaic efficiency for formic acid at a lower potential [94]. The electrode was prepared through the electrodeposition method, briefly, copper plate, copper gauze and copper sulfate were used as the working electrode, counter electrode and electrolyte respectively. A potential of – 6.0 V was applied with different structures of electrode obtained through varying time, this is shown in Fig. 13. The Faradaic efficiency for formate reached 29% at -1.1 V vs. Ag/AgCl on 60 s electrodeposited copper foam (highest value at copper).

XRD results indicated that the amount of (200) facet was 22% higher in the copper foam than in the normal copper foil, which may determine the high selectively for formate. This study indicates that the products formed in the electrochemical reduction of CO_2 are greatly related to the microstructure, particularly, which crystal faces are exposed to the reactants. Selective adsorption of certain species or intermediates may change the reaction process thus the final products are also different.

Recently, Guo *et al.* reported Cu-CDots nanocorals as a highly efficient catalyst for CO_2 reduction to formate [95]. The overpotential for the reduction of CO_2 to formate on this catalyst was only 0.13 V. Furthermore, the total Faradaic efficiency of the CO_2 reduction products was 79% (including formate (68%) and methanol) at -0.7 V vs. RHE in 0.5 M $KHCO_3$. This study provides a possibility for conversion of CO_2 into formate with high efficiency while using low-cost Cu as the electrocatalyst.

2.1.6. Carbon-based catalysts

Carbon based materials are commonly used for water oxidation [96] and oxygen reduction [97, 98] reactions due to their high surface area, low cost and significant electrocatalytic activity. Very recent studies have demonstrated the ability of carbon materials as electrocatalyts for CO_2 reduction, with CO being the majority product [99-101]. For example, Kumar *et al.* applied metal-free carbon nanotube fibres (CNF) for CO_2 reduction in an ionic liquid [101]. The CNF exhibited an exceptionally higher current density when compared to that of bulk Ag for the conversion of CO_2 to CO. In addition, nitrogen-doped carbon nanotubes have been shown to be a promising catalyst

for CO_2 reduction to CO [99, 100]. Interestingly, it was found that the polyethylenimine (PEI) functioned nitrogen-doped carbon nanotubes could reduce CO_2 to formate in aqueous media [102]. In 0.1 M $KHCO_3$ solution at -1.8 V vs. SCE, a current density of 9.5 mA cm^{-2} was reached with 87% faradaic efficiency towards formate. This excellent performance could be attributed to the synergistic effect of Nitrogen-doping as well as a PEI overlayer. Besides the carbon nanotube, graphene also exhibits good performance for selective reduction CO_2 to formate. Wang *et al.* were first to report nitrogen-doped graphene for the reduction of CO_2 to formate in an aqueous electrolyte [103]. The doping of nitrogen remarkably enhanced the current density, faradaic efficiency and stability for conversion of CO_2 to formate. Other heteroatom-doped graphene such as boron-doped graphene (BG) was developed for the selective electroreduction of CO_2 to formate [104]. The boron-doping introduces asymmetric spin density in the graphene, favouring the CO_2 adsorption on BG thus promoting the CO_2 reduction to foamte. The results showed that under -1.4 V vs. SCE in 0.1 M $KHCO_3$, a faradaic efficiency of 66% was obtained.

2.1.7. Other inorganic catalysts

Cobalt is an uncommon catalyst for the electroredution of CO_2 into formate, but Gao *et al.*'s work has shown that the electrocatalytic activity of thin layers of Co_3O_4 can be greatly increased when the thickness is reduced to below 2 nm [105]. An activity 20 times higher was obtained on the 1.72 nm thick Co_3O_4 than that of the bulk, and the formate efficiency remained at over 60% for 20 h. They also fabricated a partially

oxidized four-atom-thick cobalt layer in 2016 [106], it was found that the atomically thin layer exhibited a higher intrinsic activity and selectivity towards formate production. Moreover, the partial oxidation of the atomic layers could further improve the intrinsic activity, performing current densities about 10 mA cm^{-2} over 40 hours at -0.85 V vs. SCE, with approximately 90% formate selectivity. Their recent studies revealed that the presence of oxygen(II) vacancies in Co_3O_4 single-unite-cell layers could favor the rate-limiting proton transfer step for CO2 reduction to formate, thus accelerating the speed of CO_2 reduction [107].

Recently, Kortlever *et al*. developed a reversible catalyst by electrodepositing palladium on a polycrystalline platinum substrate [108]. The catalyst could reduce bicarbonate to formic acid at a low over-potential while also being able to directly reduce CO_2 at more negative potentials. Moreover, the catalyst exhibited reversible formic acid oxidation properties. Palladium nanoparticles at sizes of 3.8-10.7 nm were synthesized for formate production from CO_2 [109]. The faradaic efficiency of formate on 3.8 nm Pd was 86% while 98% was observed on 6.5 nm Pd. Isaacs *et al*. reported that CO_2 could be electrochemically reduced to formic acid by metal complex catalysts such as polymeric M-tetrakis aminophthalocyanines (M = Co, Ni) and hexa-aza-macrocycle complexes (Co, Ni, Cu) [110, 111]. The experiments indicated that the metallic center affected the kinetics of polymerization and the polymer morphology therefore determining the final product [111]. It was also found that electrodes based on Fe supported on carbon black (Vulacan XC-72R) could convert CO_2 to formic acid [112-114]. In 2008, Reda *et al*. found that a tungsten-containing formate dehydrogenase

enzyme (FDH1) adsorbed to an electrode surface could electrochemically convert CO_2 to formate [115]. Formate was the only product with only a very small over potential required with FDH1 (Table 2), making it a promising method for practical application. A novel synthesis of formic acid was developed in a room temperature ionic liquid via the reaction of electro-activated CO_2 and protons on pre-anodized platinum [81]. Strong acid bis(trifluoromethane)-sulfonimide ($H[NTf_2]$) was investigated on a platinum (Pt) microelectrode , 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[C_2mim][NTf2]$) was used to reduce CO_2, and formic acid was the main product with H_2 as the only side product.

In summary, the representative work on inorganic electrocatalyts for CO_2 reduction to formate/formic acid is shown in Table 3. The table includes the catalyst type, working potential, electrolyte, faradaic efficiency and current density. Among the reported metal and oxide cathodes towards formic acid production, tin, tin oxides and Co_3O_4 seem to be the best choices in terms of cost and selectivity. Moreover, the heteroatom-doped carbon materials have shown promise as robust metal-free catalysts for the next generation of catalysts.

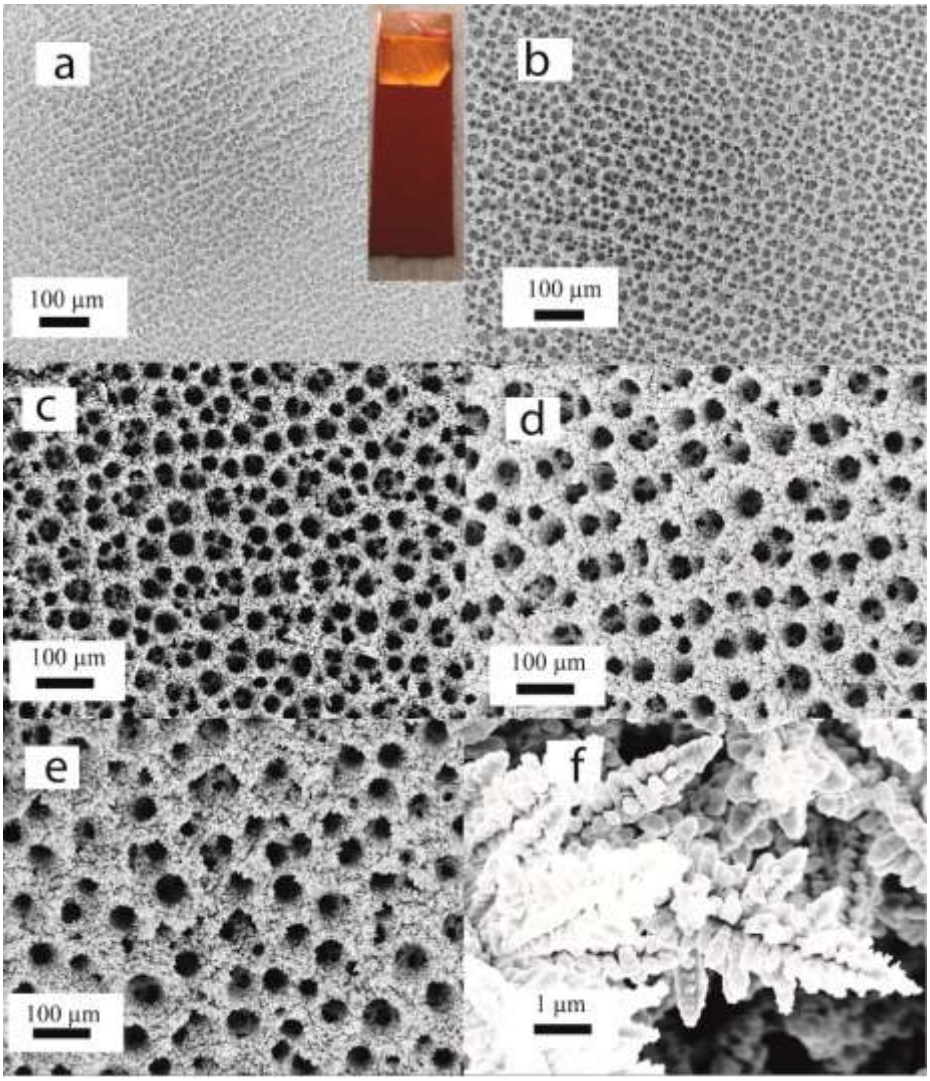

Fig. 13. SEM images of electrodeposited copper foams on a copper substrate for (a) 5s; (b) 10s; (c) 15s; (d) 30s; and (e) 60s; (f) nanostructure of the electrodeposited foams. Inset of (a) is a photo of a copper electrode immediately after electrodeposition of the copper foam [94].

Table 2 Quantitative electrochemical reduction of CO_2 to formate catalyzed by FDH1 [115].

Applied potential, V	Faradaic efficiency, %
-0.41	102.1 ± 2.2
-0.51	98.6 ± 3.6
-0.61	98 ± 1.7
-0.81	97.3 ± 1.1

2.2. Effects of electrolyte

Besides the electrocatalysts themselves, other factors such as the electrolyte, temperature and pressure are also crucial for the electrochemical reduction of CO_2 into formic acid or formate. The type of electrolyte frequently used in electroreduction of CO_2 can be roughly classed into aqueous and non-aqueous solutions. The non-aqueous electrolytes such as ionic liquids have been studied for the electroreduction of CO_2 due to their high CO_2 solubility, wide potential window and extremely low volatility. Martindale and Compton applied $H[NTf_2]$ dissolved in $[C_2mim][NTf_2]$ as an electrolyte for the electroreduction of CO_2 to HCOOH with a Pt electrode [81]. In $BMIMBF_4$, CO_2 was reduced on a Cu electrode at -2.4 V vs Ag/AgCl at room temperature [116]. Snuffin *et al.* synthesized a novel ionic liquid $EMIMBF_3Cl$ which performed at a high current density for CO_2 reduction at -1.8 V vs. silver wire with a Pt electrode [117]. The use of non-aqueous electrolyte mtetrabutylammonium perchlorate (TBAP) in methanol makes the electrochemical reduction of CO_2 to formic acid and acetic acid at low over-

potentials possible, such as, -0.3 V vs. SCE (sat. KCl) when polyaniline (PANI)-Cu_2O nano-composite was used as the cathode, where the source of hydrogen was from added H_2SO_4 [118]. A large advantage of using a low over-potential is that the overall energy efficiency would be much higher, thus it is a promising approach for the electrochemical reduction of CO_2 into hydrocarbons [50]. However, it would not be possible if the hydrogen source was changed from H_2SO_4 to H_2O as a relatively high potential is required to split water. A non-aqueous aprotic electrolyte was tried using a lead wire cathode for CO_2 reduction [119]. The propylene carbonate (PrC) containing tetraethylammonium perchlorate (TEAP) was reported as the electrolyte. Cyclic voltammetry and infrared reflectance spectroscopy confirmed that the CO_2 reduction reaction was a mass transfer process with no CO formed as an intermediate or final product under these operating conditions. This indicates the use of non-aqueous solvent TEPA-PrC can suppress the formation of CO.

In the aqueous electrolytes, many studies demonstrated that the efficiency and selectivity for CO_2 electroreduction depended on the solvent including cations and anions [120]. The Faradaic efficiency was enhanced in the presence of CO_3^{2-} and HCO_3^-, which could be due to the involvement of the anions during the electroreduction of CO_2. The Faradaic efficiency of formic acid production increased with the anions in the order: $PO_4^{3-} < SO_4^{2-} < CO_3^{2-} < HCO_3^-$. Ogura *et al.* studied the differences of Cl^-, Br^- and I^- by conducting CO_2 electroreduction in 3 M KCl, KBr and KI solution using a copper mesh electrode [121]. It revealed that the electron transferred from the adsorbed halide anion to CO_2, accelerated the CO_2 reduction. A higher halide anion adsorption to the electrode

lead to faster CO_2 conversion, forming a higher reduction current. Additionally, higher halide anion adsorption limited the proton adsorption, resulting in a more negative hydrogen evolution potential. In regard to the cations, since small cations such as Li^+ and Na^+ are strongly hydrated, they will not adsorb on the electrode thus they can take a lot of water molecules to the cathode which supplies the protons required during electroreduction. Contrary to this, large cations are not easily hydrated so they tend to adsorb on the cathode. Bhugun *et al.* reported the effects of cations for formic acid formation finding that the formic acid production decreased with increasing concentration of cations with the ability of reactivity improvement in the order of Mg^{2+} = Ca^{2+} > Li^+ > Na^+ [122]. Thorson *et al.* investigated the relationship between the size of cations and CO selectivity on silver electrodes [123], specifically, larger cations (Na^+ < K^+ < Rb^+ < Cs^+) improved the CO production while suppressing H_2 formation.

It can be concluded that [48]: the type of anions influences the pH at the electrode which then determines the proton content, thus it finally affects the reaction kinetics; cations of different sizes are adsorb on the electrode surface to a different extent, changing the electrical double layer structure and affecting the reaction kinetics and energetics. Furthermore, the solubility of CO_2 in solution is another key factor that affects the performance of the electrode, due to reduced mass transfer resistance at higher CO_2 solubilities.

2.3. The effects of temperature and pressure

Temperature and pressure are important parameters for the electrochemical

reduction of CO_2 into formic acid. It was reported that the current density was 20 times greater when the temperature changed from 275 to 333K [124]. Mizuno *et al*. found that the Faradaic efficiency for formic acid on a Pb electrode firstly increased and then decreased from 20 to 100 ^oC [125]. When it comes to Tin and Indium electrodes, the Faradaic efficiency continued to decrease from 20 to 100 ^oC. It is expected that the increase in temperature promotes all of the reaction rates, including those for the competing reactions, while also reducing the solubility of CO_2 and improving the CO_2 diffusion rate. Generally, a higher efficiency of CO_2 electroreduction can be obtained at a lower temperature.

The solubility of CO_2 can be improved with higher pressure. From this point of view, higher pressures are better for CO_2 electroreduction with the current density expected to be higher. Electrochemical reduction of CO_2 in aqueous solutions (both inorganic and tetraalkylammonium salts) and non-aqueous electrolytes under high pressure were investigated by Ito *et al.* in 1980s [126-128]. In 1995, Asano *et al.* studied the electrochemical reduction of carbon dioxide under high pressure on various electrodes in an aqueous $KHCO_3$ electrolyte [129]. It was found that the electrochemical reduction of CO_2 at large partial current densities was accomplished on many electrodes under a CO_2 pressure of 30 atm, e.g., 397 mA cm^{-2} on Pd and 383 mA cm^{-2} on Ag however, the Faradaic efficiency to formate on Pd and Ag was only 44% and 16% respectively. The Faradaic efficiency on Sn and Pb was 92% and 95% with high current densities of 163 and 156 mA cm^{-2} respectively [129], indicating that Pb and Sn are good cathode materials for the electrochemical reduction of CO_2 to formic acid at high pressure.

Todoroki *et al.* explored the electroreduction of CO_2 with In, Pb and Hg under high pressure in an aqueous solution [130]. The Faradaic efficiency of formate grew with rising pressure, with the value increasing past 90% at 20atm. As the pressure continuously increased, the rate-determining step of the reaction changed from CO_2 diffusion to electron transfer at the electrode surface. Recently, electrochemical reduction of CO_2 into formic acid under high pressure at a Sn cathode in an aqueous KCl or Na_2SO_4 electrolyte was investigated. It was found that the Faradaic efficiency decreased against time, this is possibly due to the anode oxidation of the formed formic acid [131].

Table 3. Summary of electrocatalysts for CO_2 reduction to formate.

Catalysts	Potential	Electrolyte	Formate Faradaic efficiency (%)	Current density (mA cm^{-2})	Ref.
Pb wire	-2.0 V vs. Ag/AgCl	0.3 M KOH in methanol 15 ºC	66	4	[54]
Pb granule	-1.8 V vs. SCE	0.2 M K_2CO_3 50 bar 80 ºC	94	0.72	[56]
Lead on stainless steel	-1.8 V vs. anode	Catholyte: 0.2 M K_2HPO_4 + H_3PO_4 pH 7 Anolyte: 0.2 M KOH	93	2	[32]
Electrodeposited porous Pb on Cu plate	-1.7 V vs. SCE	0.5 M $KHCO_3$ 5 ºC	96.8	N/A	[57]
Nanolayered Pb		0.1 M $KHCO_3$ 5 ºC	94.1	N/A	[58]
Lead foil	-1.83 V vs. SCE	0.5 M NaOH 4 ºC	90	2.5	[39]
Pb plate	n/a	Catholyte: 0.45 M KHCO3 + 0.5 M KCl Anolyte: 1 M KOH	57	10.5	[59]
Metallic Pb	-2.4 V vs. Ag/AgCl	0.1 M TEAP/H_2O 100 ºC	78.9	N/A	[132]
Tin foil	-1.8 V vs. Ag/AgCl	0.1 M $KHCO_3$	91	2.5	[62]
Tin foil	-2.0 V vs. SCE	0.5 M KHCO3	63.49	28	[133]
Tin gas diffusion electrode (GDE)	-1.8 V vs. Ag/AgCl	0.5 M $KHCO_3$	72.99	13.45	[67]
Reduced Nano-SnO_2/graphene	-1.8 V vs. SCE	0.1 M $NaHCO_3$	93.6	10.2	[69]
Tin quantum sheets confined in graphene	-1.8 V vs. SCE	0.1 M $NaHCO_3$	89	21.1	[68]
Tin dendrite	-1.36 V vs. RHE (-2.0 V vs. SCE)	0.1 M $KHCO_3$	71.6	17.1	[134]
Tin/tin oxide thin film	-0.7 V vs. RHE	0.5 M $NaHCO_3$	40	1.7	[38]
3.5 nm thickness of SnOx of tin nanoparticles	-1.2 V vs. CE	0.1 M $KHCO_3$	64	3	[74]
Porous SnO_2/carbon cloth	-1.6 V vs. Ag/AgCl	0.5 M $NaHCO_3$	87	45	[76]
Sn-Nafion coated	-1.6 V vs. NHE	0.5 M $NaHCO_3$	70	27	[66]
Indium disc	-1.9 V vs. Ag/AgCl	[Emim][TFA] + 33% H_2O	>90	3.5	[83]

Zn	-1.5 V vs. anode	0.5 M $KHCO_3$	78.54	<2	[86]
Ultrathin Co_3O_4 (1.72 nm)	-0.88 V vs. SCE	0.1 M $KHCO_3$	64.3	0.68	[105]
Partially oxidized atomic cobalt	-0.85 V vs. SCE	0.1 M $NaSO_4$	90.1	~10	[106]
Cu nanofoam	-1.1 vs. Ag/AgCl	0.1 M $KHCO_3$	29	~10	[94]
Cu-CDots nanocorals	-0.7V vs. RHE	0.5 M $KHCO_3$	68	~4.2	[95]
Nitrogen-doped graphene	-0.84 vs. RHE	0.5 M $KHCO_3$	73	7.5	[103]
Boron-doped graphene	-1.4 V vs. SCE	0.1 M $KHCO_3$	66	~1.5	[104]
Tungsten-containing formate dehydrogenase enzyme (FDH1)	-0.41 ~ -0.81 V	0.02 M Na_2CO_3	~100	N/A	[135]
$[Fe_4S_4(SR)_4]^{2-}$	-1.7 V	DMF	59	N/A	[136]
$[Ru(bpy)_2(CO)_2]_2+$	-1.3 V vs. SCE	Saturated H_2O/DMF (9 : 1, v/v) solution in the presence of Me_2NH· HCl, pH 9.5	84.3	3.3	[137]
$[(bpy)_2Ru(dmbbbpy)](PF_6)_2$ (dmbbbpy = 2,2'-bis(1-methylbenzimidazol-2-yl)-4,4'-bipyridine)	-1.65 V vs. Ag/AgCl	MeCN + 2.5% H_2O	89	N/A	[138]
$[(bpy)_2Ru(dmbbbpy)Ru(bpy)_2](PF6)_4$	-1.55 V vs. Ag/AgCl	MeCN + 2.5% H_2O	90	N/A	[138]
Iridium(III) trihydride complex (POCOP)IrH_2 POCOP = C_6H_3-2,6-$(OP^tBu_2)_2$	-1.73 V vs. Fc/Fc^+	MeCN + 12% H_2O	>99	N/A	[139]
$Pd_{70}Pt_{30}$/C	-0.4 V vs. RHE	0.1 M KH_2PO_4 / 0.1 M K_2HPO_4 pH 6.7	88	5	[140]

3. Challenges and future opportunities

Large amounts of CO_2 will be available in the following decades as fossil fuels are

still currently the most important energy resources on earth. With the possible application of CO_2 capture processes, it is desired to find an outlet for the captured CO_2. Also, the demand for formic acid will be booming with the development of a global economy. Electrochemical reduction of CO_2 to formic acid is therefore a useful technology to solve these problems. The combination of CO_2 capture and electrochemical reduction of CO_2 can be used for renewable electricity storage as well.

As discussed above, many catalysts have been developed in order to achieve a high conversion. Among the reported metal and oxide cathodes towards formic acid production, tin and tin oxides have proven to be best choices in terms of cost and selectivity. However, there are still several challenges limiting the practical applications. (1) low catalyst activity, (2) low selectively, (3) low catalyst stability. It is obvious that the overpotential for catalysts in CO_2 electroreduction is normally too high meaning that their activities are poor and thereby exhibit low energy efficiencies. Although some of the catalysts exhibited high selectively, their stability is not high enough for industrial-scale application. Normally, the stability test carried out in the literature is less than one hundred hours with longer term stability tests not yet reported. The active sites on the electrode could be blocked by the intermediates or by-products produced during the CO_2 reduction, leading to the degradation of catalyst activity. For cells not divided by a separation membrane, anode oxidation of the produced formic acid will also reduce the efficiency.

In conclusion, electroreduction of CO_2 to formic acid or formate is still at an early stage with many issues that need to be solved. To overcome these challenges and reach

the requirements for commercialization, several directions should be focused on in the future: (1) Exploration of new cathode catalysts. Several metals and oxides such as tin / tin oxide are good cathode catalysts with high selectivity to formic acid. Some progress has been made but the technology is still not sufficient for large scale use. Therefore, the next generation of novel catalysts might be obtained through a combination of the existing materials as well as the tailoring of the catalyst microstructure. The combined materials could demonstrate different properties from individual components due to the mutual effect of each substance. Catalysts with high activity, low over-potential, high selectivity and good stability may be obtained by optimizing the compositions and other important parameters such as particle size. The desired number of active sites could be increased by tailoring the micro-structure of these materials. Materials with different micro-structures may have different selectivities and catalytic properties when prepared through different methods. For electrodeposited metal catalysts, the selectivity is greatly related to the current density and deposit time leading to various microstructures, thus various active faces may be exposed to CO_2 and H_2O resulting in different products. Simultaneously，the surface area and mass transport property would also be changed which may form ideal catalysts for CO_2 reduction. Additionally, the electrolyte and working conditions such as temperature and pressure should be optimised according to the designed electrode. (2) Further understanding of the reaction mechanisms. The studies on the CO_2 conversion mechanisms are insufficient presently [141], although some of the literature has attempted to explore the fundamentals using both experimental and theoretical

modelling methods [142, 143]. A better understanding of the fundamental mechanisms will significantly help researchers in optimizing the operation conditions of the catalyst directly improving its performance. This will also help to identify better electrocatalysts for CO_2 reduction to formic acid. (3) To explore suitable anodes for two-electrode cells that can be used for real applications. Most of the research activities on electrochemical reduction of CO_2 to formate/formic acid focus on three–electrode cells, however, two-electrode cells are used for real commercial applications. Therefore, it is desired to explore suitable anodes for both acidic and alkaline environments which can be used as a matched electrode in order to build two electrode cells. Formic acid production rate, Faradaic and overall energy efficiencies, and long term stability of the two electrode cells are important parameters that need to be investigated in order to achieve real applications of this technology,. With the efforts of researchers in the areas of catalysis, electrochemistry, materials science and other relevant areas, electrochemical synthesis will provide a low carbon and sustainable process for production of useful hydrocarbons, such as formic acid.

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